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Effects of Milling Time on the Hydrogen Storage Properties of Mg-based Transition Metals-added Alloys

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In this work, Mg was employed as a starting material. Ni, Fe and Ti were selected as additives to improve hydriding and dehydriding rates of Mg. A 90 wt.% Mg + 5 wt.% Ni + 2.5 wt.% Fe + 2.5 wt.% Ti sample [named 90Mg-Ni-Fe-Ti (8 h)] was prepared by mechanical grinding under H_2 atmosphere (reactive mechanical grinding) for 8 h, using a planetary ball mill. The hydrogen-storage properties of the prepared sample were then investigated and compared with those of a 90 wt.% Mg + 5 wt.% Ni + 2.5 wt.% Fe + 2.5 wt.% Ti sample previously studied by preparing via reactive mechanical grinding for 4 h [named 90Mg-Ni-Fe-Ti (4 h)]. Reactive mechanical grinding for a longer time (for 8 h), compared with that for 4 h, intensified the effects of reactive mechanical grinding. After activation, 90Mg-Ni-Fe-Ti (4 h) had higher initial hydriding and dehydriding rates and larger quantities of hydrogen absorbed and released for 60 min than 90Mg-Ni-Fe-Ti (8 h). Prolonged milling (for example, for 8 h) is considered to bring about coalescence of particles which is caused by severe plastic deformation of ductile Mg particles. The stronger effect of hydriding-dehydriding cycling and the less compact agglomeration are believed to lead to the higher initial hydriding and dehydriding rates and the larger quantities of hydrogen absorbed and released for 60 min of 90Mg-Ni-Fe-Ti (4 h) than those of 90Mg-Ni-Fe-Ti (8 h) after n = 2.

Keywords: hydrogen absorption and desorption kinetics, Mg-Ni-Fe-Ti, reactive mechanical grinding, milling conditions, microstructure.

1. INTRODUCTION

Storing hydrogen as a gas, liquid hydrogen storage, the physisorption of hydrogen, and storing it in the form of metal hydrides, complex hydrides, and via chemical reactions are currently studied [1].

Magnesium, one of the prospective hydrogen storage materials, has a high hydrogen storage capacity of about 7.6 wt.% and is abundant in the earth's crust. However, its hydrogen absorption and desorption kinetics are very slow and occur at very high temperatures (at least 623 ~ 673 K and over a period of several hours).

Many studies have been conducted in an attempt to improve the reaction kinetics of magnesium with hydrogen by adding some catalytic materials and performing mechanical treatment and/or alloying. For example, elements Pd [2], Ti [3], Co, Ni, or Fe [4, 5], Ni, Fe, and/or Ti [6 – 8], graphite [9, 10], and transition metals and/or compounds to Mg or MgH_2 [11 – 18] were added. Nucleation can be facilitated by creating active nucleation sites and defects; these are made by mechanical treatment and/or alloying with additives [19]. The diffusion distance of hydrogen can be decreased by the mechanical treatment and/or alloying of Mg with additives, thereby reducing the magnesium particle size [20]. In addition, the hydrogen mobility can be improved by additives that create microscopic paths of hydrogen [20]. Consequently, a rough surface of magnesium possessing many cracks and defects is considered more advantageous for hydrogen absorption [21].

As a process of mechanical treatment and/or alloying with additives, we chose mechanical grinding under H_2 atmosphere (reactive mechanical grinding), which is expected to create defects, produce paths of hydrogen, and decrease particle size. We were in particular interested in the milling time, one of the important factors of reactive mechanical grinding.

In this work, Mg was used as a starting material. Ni, Fe and Ti were chosen as additives to enhance hydriding and dehydriding rates of Mg. Ni is known to form Mg_2NiH_4 which has higher hydriding and dehydriding rates than magnesium. Fe is cheap as compared with Ni, and may act active site for the dissociative chemisorption of H_2 [22]. Ti is believed to increase the hydriding and dehydriding rates when it was added. A 90 wt.% Mg+5 wt.% Ni+2.5 wt.% Fe+2.5 wt.%Ti sample [named 90Mg-Ni-Fe-Ti (8 h)] was prepared by reactive mechanical grinding for 8 h, using a planetary ball mill. The hydrogen-storage properties of the prepared sample were then investigated and compared with those of a 90 wt.% Mg+5 wt.% Ni+2.5 wt.% Fe+ +2.5 wt.% Ti sample [23] previously studied by preparing via reactive mechanical grinding for 4 h [named 90Mg-Ni-Fe-Ti (4 h)].

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2. EXPERIMENTAL DETAILS

The starting materials were pure Mg (particle size 75 – 150 μm, purity 99.6 %), Ni (average particle size 2.2 ~ 3.0 μm, purity 99.9 %), Fe (particle size < 10 μm, purity 99.9 %), and Ti (particle size < 45 μm, purity 99.98 %) powders. Mg, Ni and Fe powders were purchased from Alfa Aesar GmbH (Germany), and Ti powder was provided by Sigma-Aldrich (USA).

In our previous work, the optimum conditions for reactive mechanical grinding were the sample weight to ball weight ratio of 1/45 and a disc revolution speed of 250 rpm [24]. These powders were mixed to obtain the composition 90 wt.% Mg+5 wt.% Ni+2.5 wt.% Fe+ +2.5 wt% Ti. The total weight of the mixture was 8 g. The mixture was put into a stainless steel container with 105 hardened steel balls (total weight: 360 g), and the container with a volume of 250 ml was then sealed hermetically. All handling was performed in a glove box filled with Ar. Mechanical grinding was performed in a planetary ball mill at a disc revolution speed of 250 rpm under 12 bar H_2. After repeating milling for 15 min and pausing for 5 min four times, the container was refilled with hydrogen up to a pressure of 12 bar H_2. Milling, pausing, and refilling of hydrogen were repeated, leading to the total milling time of 8 h.

The quantities of hydrogen absorbed or released were measured as a function of time in a Sieverts' type apparatus [24] under nearly constant hydrogen pressures. The powders as-milled and after hydriding-dehydriding cycling were characterized by X-ray diffraction (XRD), using a Rigaku D/MAX 2500 powder diffractometer with Cu Kα radiation. The microstructures of the particles were observed by a JSM-6400 scanning electron microscope (SEM) operated at 20 kV.

3. RESULTS AND DISCUSSION

The absorbed hydrogen quantity is expressed as the percentage of the absorbed hydrogen with respect to the sample weight. Fig. 1 shows the absorbed hydrogen quantity vs. time curves at 573 K under 12 bar H_2 at the number of cycles of one (n = 1) for the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples.

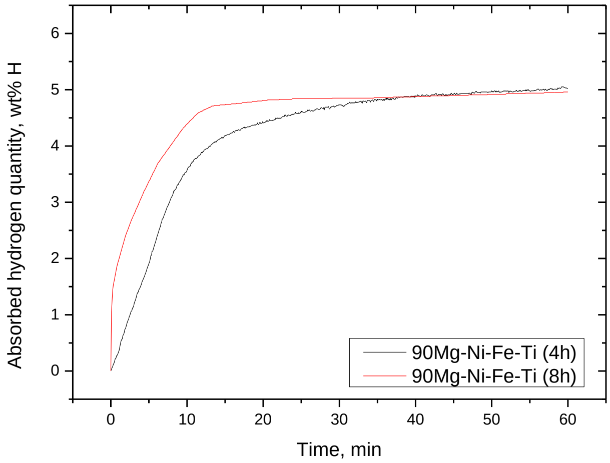


Fig. 1. Absorbed hydrogen quantity vs. time curves at 573 K under 12 bar H_2 at n = 1 for the 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples

The times of reactive mechanical grinding for the 90Mg-Ni-Fe-Ti samples were 4 h and 8 h, respectively. For the 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples the hydriding rates are quite high in the beginning and then it gets gradually lower. 90Mg-Ni-Fe-Ti (8 h) has a higher initial hydriding rate but a slightly smaller quantity of hydrogen absorbed for 60 min than 90Mg-Ni-Fe-Ti (4 h). 90Mg-Ni-Fe-Ti (8 h) absorbs 3.37 wt.% H for 5 min, 4.39 wt.% H for 10 min, and 4.96 wt.% H for 60 min. About 67.9 % of the hydrogen absorbed for 60 min is absorbed for 5 min.

The released hydrogen quantity is also expressed as the percentage of the released hydrogen with respect to the sample weight. The released hydrogen quantity vs. time curves at 573 K under 1.0 bar H_2 at n = 1 for the 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples are shown in Fig. 2. The 90Mg-Ni-Fe-Ti (8 h) sample exhibits quite low dehydriding rate, compared with the 90Mg-Ni-Fe-Ti (4 h). 90Mg-Ni-Fe-Ti (4 h) has a relatively high initial dehydriding rate and then its dehydriding rate decreases gradually from about 25 min. 90Mg-Ni-Fe-Ti (4 h) releases 0.52 wt.% H for 5 min, 1.09 wt.% H for 10 min, 2.36 wt.% H for 20 min, and 4.20 wt.% H for 60 min.

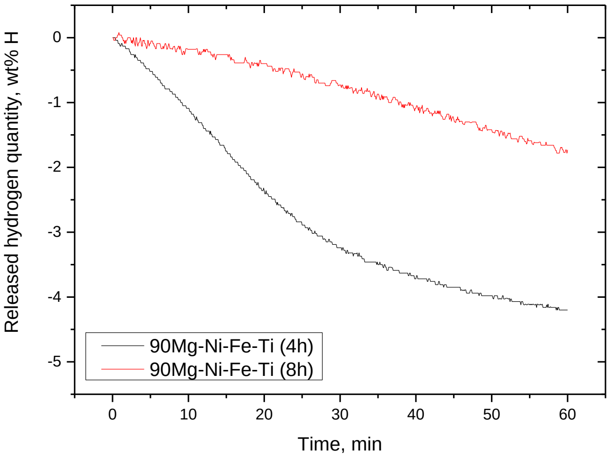


Fig. 2. Released hydrogen quantity vs. time curves at 573 K under 1.0 bar H_2 at n = 1 for the 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples

At n = 1, 90Mg-Ni-Fe-Ti (4 h) has a lower initial hydriding rate and a slightly larger quantity of hydrogen absorbed for 60 min than 90Mg-Ni-Fe-Ti (8 h), whereas 90Mg-Ni-Fe-Ti (4 h) has a higher initial dehydriding rate and a larger quantity of hydrogen released for 60 min than 90Mg-Ni-Fe-Ti (8 h). This is thought to be due to the expansion of the Mg lattice by hydriding reaction at the first cycle, which separates particles and thus provides the passages for hydrogen.

Table 1 gives the absorbed and released hydrogen quantities (AHQ and RHQ) of the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples at n = 1 after 5, 10, 20, 30 and 60 min for absorption at 573 K under 12 bar H_2 and for desorption at 573 K under 1.0 bar H_2.

The hydriding rates of the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples are quite high in the beginning. For 90Mg-Ni-Fe-Ti (8 h), about 67.9 % of the hydrogen absorbed for 60 min is absorbed for 5 min. The hydrogen quantities absorbed for 5 min by these two samples are compared. Fig. 3 presents the variations, with the number of hydriding-dehydriding cycles, of the hydrogen quantity absorbed for 5 min [AHQ (5 min)] at 573 K under 12 bar H_2 for 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h).

Table 1. Absorbed and released hydrogen quantities (AHQ and RHQ) of the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples at n = 1 after 5, 10, 20, 30 and 60 min for absorption at 573 K under 12 bar H_2 and for desorption at 573 K under 1.0 bar H_2

Sample	AHQ/RHQ, wt.% H				
	5 min	10 min	20 min	30 min	60 min
90Mg-Ni-Fe-Ti (4 h)	1.91/0.52	3.57/1.09	4.41/2.36	4.73/3.24	5.02/4.20
90Mg-Ni-Fe-Ti (8 h)	3.37/0.09	4.39/0.18	4.81/0.40	4.85/0.73	4.96/1.73

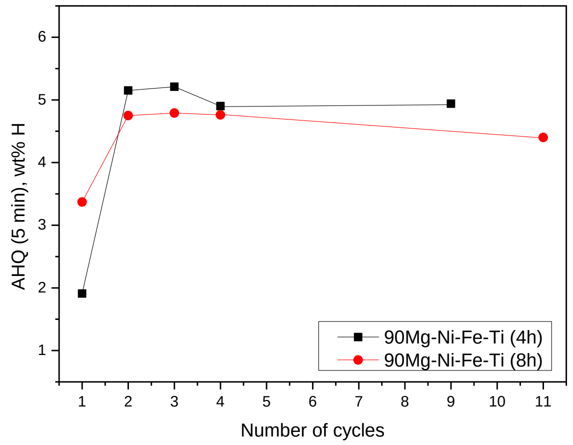


Fig. 3. Variations, with the number of hydriding-dehydriding cycles, of the hydrogen quantity absorbed for 5 min [AHQ (5 min)] at 573 K under 12 bar H_2 for the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples

At n = 1, 90Mg-Ni-Fe-Ti (8 h) absorbs a larger amount of hydrogen for 5 min than 90Mg-Ni-Fe-Ti (4 h), absorbing 3.37 and 1.91 wt.% H, respectively. As the number of hydriding-dehydriding cycles increases, the absorbed hydrogen quantities of 90Mg-Ni-Fe-Ti (8 h) and 90Mg-Ni-Fe-Ti (4 h) increase and then decrease from n = 3. A rapid increase in AHQ (5 min) from n = 1 to n = 2 is believed due to the expansion of the Mg lattice by hydriding reaction, causing separation of particles and thus providing the passage for hydrogen.

The fractions of the hydrogen quantities released for 30 min by the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples are quite large. The hydrogen quantities released for 30 min by these two samples are compared. The variations, with the number of hydriding-dehydriding cycles, of the hydrogen quantity released for 30 min [RHQ (30 min)] at 573 K under 1.0 bar H_2 for the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) are shown in Fig. 4. 90Mg-Ni-Fe-Ti (4 h) releases a larger amount of hydrogen for 30 min than 90Mg-Ni-Fe-Ti (8 h), releasing 3.24 and 0.73 wt.% H, respectively, at n = 1. As the number of hydriding-dehydriding cycles increases, the released hydrogen quantities increase, those of 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) reaching the maximum values of 3.67 wt.% H (at n = 4) and 2.99 wt.% H (at n = 3), respectively.

Fig. 3 and Fig. 4 show that the effects of of hydriding-dehydriding cycling on the hydriding and dehydriding rates of 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) are very strong from n=1 to n=2. The complete activation of these two samples was achieved after about three hydriding-dehydriding cycles. The relatively higher initial hydriding rate at n = 1 of 90Mg-Ni-Fe-Ti (8 h), compared with that of 90Mg-Ni-Fe-Ti (4 h), proves that, the effect of reactive mechanical grinding on the hydriding rates of 90Mg-Ni-Fe-Ti (8 h) is stronger than that on those of 90Mg-Ni-Fe-Ti (4 h). On the other hand, the relatively rapid increase in the value of AHQ (5 min) for 90Mg-Ni-Fe-Ti (4 h) as the number of cycles increases from n = 1 to n = 2 supports that, the effect of hydriding-dehydriding cycling on the hydriding rates of 90Mg-Ni-Fe-Ti (4 h) is stronger than that for 90Mg-Ni-Fe-Ti (8 h).

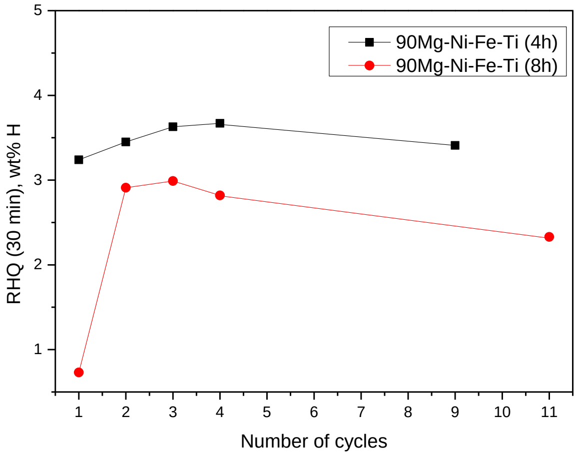


Fig. 4. Variations, with the number of hydriding-dehydriding cycles, of the hydrogen quantity released for 30 min [RHQ (30 min)] at 573 K under 1.0 bar H_2 for the 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples

Fig. 5 presents the absorbed hydrogen quantity vs. time curves at 573 K under 12 bar H_2 for the activated 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples.

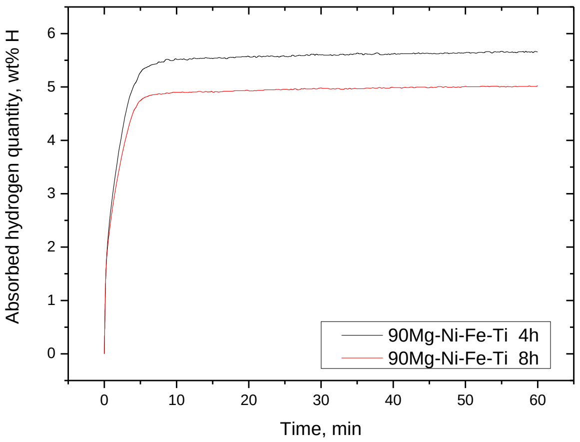


Fig. 5. Absorbed hydrogen quantity vs. time curves at 573 K

under 12 bar H_2 for the activated 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples

The hydriding rate is very high in the beginning up to about 5 min. The hydriding rate then decreases rapidly, and after about 5 min the hydriding rate is extremely low. 90Mg-Ni-Fe-Ti (4 h) has a higher initial hydriding rate and a larger absorbed hydrogen quantity for 60 min than 90Mg-Ni-Fe-Ti (8 h). The activated 90Mg-Ni-Fe-Ti (4 h) sample absorbs 5.21 wt.% H for 5 min, 5.50 wt.% H for 10 min, 5.56 wt.% H for 20 min, 5.62 wt.% H for 30 min, and 5.67 wt.% H for 60 min. About 91.9 % of the hydrogen absorbed for 60 min is absorbed for 5 min.

The released hydrogen quantity vs. time curves at 573 K under 1.0 bar H_2 for the activated 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples are shown in Fig. 6. 90Mg-Ni-Fe-Ti (4 h) sample has a higher initial dehydriding rate and a larger released hydrogen quantity for 60 min than 90Mg-Ni-Fe-Ti (8 h). The activated 90Mg-Ni-Fe-Ti (4 h) sample releases 0.52 wt.% H for 5 min, 1.09 wt.% H for 10 min, 2.49 wt.% H for 20 min, 3.63 wt.% H for 30 min, and 4.72 wt.% H for 60 min.

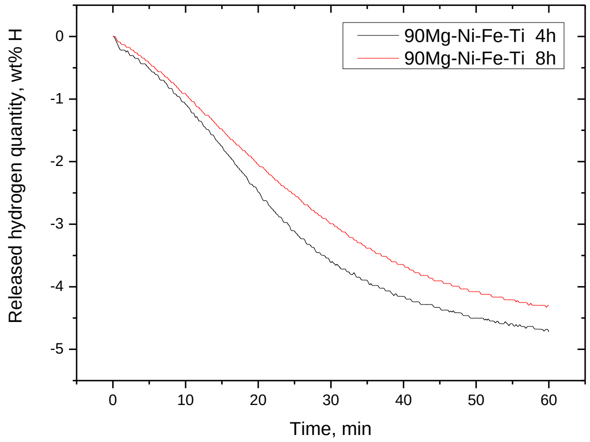


Fig. 6. Released hydrogen quantity vs. time curves at 573 K under 1.0 bar H_2 for the activated 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples

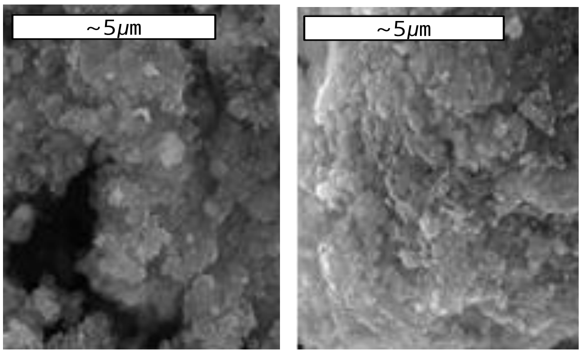
Table 2 shows the absorbed and released hydrogen quantities (AHQ and RHQ) of the activated 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after 5, 10, 20, 30 and 60 min for absorption at 573 K under 12 bar H_2 and for desorption at 573 K under 1.0 bar H_2.

Table 2. Absorbed and released hydrogen quantities (AHQ and RHQ) of the activated 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after 5, 10, 20, 30 and 60 min for absorption at 573 K under 12 bar H_2 and for desorption at 573 K under 1.0 bar H_2

Sample	AHQ/RHQ, wt.% H				
	5 min	10 min	20 min	30 min	60 min
90Mg-Ni-Fe-Ti (4 h)	5.21/0.52	5.50/1.09	5.56/2.49	5.62/3.63	5.67/4.72
90Mg-Ni-Fe-Ti (8 h)	4.75/0.43	4.90/0.91	4.93/2.04	4.99/2.99	5.02/4.30

Fig. 7 exhibits the microstructures, observed by SEM, of the activated 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples. The 90Mg-Ni-Fe-Ti (8 h) sample has fine particles. The 90Mg-Ni-Fe-Ti (4 h) sample has slightly larger particles than the 90Mg-Ni-Fe-Ti (8 h) sample. The particles of the samples are agglomerated. However, the particles of the 90Mg-Ni-Fe-Ti (8 h) sample are agglomerated more compactly than the 90Mg-Ni-Fe-Ti (4 h) sample. The 90Mg-Ni-Fe-Ti (4 h) has some cracks.

The XRD patterns of the dehydrided 90Mg-Ni-Fe-Ti (4 h) [23] and 90Mg-Ni-Fe-Ti (8 h) samples after activation are presented in Fig. 8. All the samples contain Mg, $H_{0.3}Mg_2Ni$, MgH_2, MgO, and Fe phases [25].



a b

Fig. 7. Microstructures, observed by SEM, of the activated: a – 90Mg-Ni-Fe-Ti (4 h); b – 90Mg-Ni-Fe-Ti (8 h) samples

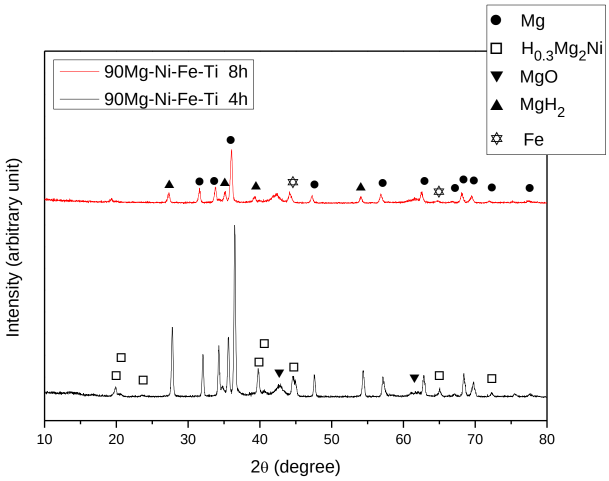


Fig. 8. XRD patterns of the dehydrided 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after activation

Mg_2NiH_4, which has higher hydriding and dehydriding rates than magnesium [6], is believed to be formed after reactive mechanical grinding and hydriding reaction, by a reaction among Ni, Mg, and hydrogen. Mg_2NiH_4 then forms $H_{0.3}Mg_2Ni$ after dehydriding reaction. The phases related to Ti could not be found, probably due to its small content. The added Ti was reported to form Ti hydride [11], which is brittle. The titanium hydride can be pulverized during reactive mechanical grinding and this pulverized titanium hydride can help Mg pulverized into finer particles. The titanium hydride can prevent the magnesium from being agglomerated by staying as a hydride among Mg particles.

In order to calculate the crystallite size and strain of Mg in the dehydrided samples after hydriding-dehydriding cycling, the Williamson-Hall method [23] is applied in which the following equation was used:

$$B \cos\theta = K \lambda / t + 4 \varepsilon \sin\theta, \qquad (1)$$

where B is full width at half maximum (FWHM); K shape factor (0.9); λ wavelength (1.54056 Å), t crystallite size, and ε strain. The crystallite sizes of Mg in the dehydrided 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after hydriding-dehydriding cycling were 49.7 and 37.0 nm, respectively. The strains of Mg in the dehydrided 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after hydriding-dehydriding cycling were 0.0088 and 0.0407 %, respectively. The order of the crystallite sizes of Mg in the dehydrided 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after hydriding-dehydriding cycling is the same as that of the particle sizes observed by SEM (Fig. 7).

As mentioned above, the effect of reactive mechanical grinding on the hydriding rates of 90Mg-Ni-Fe-Ti (8 h) is stronger than that on those of Mg-5Ni-2.5Fe-2.5Ti (4 h). On the other hand, the effect of hydriding-dehydriding cycling (due to the expansion of the Mg lattice by hydriding) on the hydriding rates of 90Mg-Ni-Fe-Ti (4 h) is stronger than that for 90Mg-Ni-Fe-Ti (8 h). Fig. 7 shows that the 90Mg-Ni-Fe-Ti (4 h) sample has slightly larger particles than the 90Mg-Ni-Fe-Ti (8 h) sample, but the particles of the 90Mg-Ni-Fe-Ti (4 h) sample are agglomerated less compactly than the 90Mg-Ni-Fe-Ti (8 h) sample and the 90Mg-Ni-Fe-Ti (4 h) has some cracks. Prolonged milling (for example, for 8 h) is considered to bring about coalescence of particles which is caused by severe plastic deformation of ductile Mg particles. The stronger effect of hydriding-dehydriding cycling for 90Mg-Ni-Fe-Ti (4 h) may be related to the less compact agglomeration of particles of this sample. The two points (the stronger effect of hydriding-dehydriding cycling and the less compact agglomeration) are believed to lead to the higher initial hydriding and dehydriding rates and the larger quantities of hydrogen absorbed and released for 60 min of 90Mg-Ni-Fe-Ti (4 h) than those of 90Mg-Ni-Fe-Ti (8 h) after n = 2.

90 wt.% Mg+10 wt.% Ni alloy prepared by mechanical grinding in an Ar atmosphere absorbed about 4.45 wt.% H at 595 K under 11.7 bar H_2 for 4 min [26]. Song et al. [27] studied hydrogen storage properties of an 80 wt.% Mg+13.33 wt.% Ni+6.67 wt.% Fe alloy prepared via planetary ball milling in a H_2 atmosphere. After activation, the sample absorbed 5.61 wt.% H for 60 min at 593 K under 12 bar H_2 and desorbed 3.92 wt% H for 30 min at 593 K under 1.0 bar H_2. Our previous work [6] showed that 80 wt.% Mg+10 wt.% Ni+5 wt.% Fe+ +5 wt.%Ti, prepared by reactive mechanical grinding, was activated after two hydriding–dehydriding cycles and absorbed 5.51 wt.% H under 12 bar H_2 and released 5.18 wt.% H under 1.0 bar H_2 at 573 K for 60 min. The 80 wt.% Mg+10 wt.% Ni+5 wt.% Fe+5 wt.% Ti sample absorbed a smaller amount of hydrogen and released a larger amount of hydrogen than 90Mg-Ni-Fe-Ti (4 h) under the same conditions. It is thought that a larger content of Mg_2NiH_4 in 80 wt.% Mg + 10 wt.% Ni + 5 wt.% Fe + 5 wt.% Ti than in 90Mg-Ni-Fe-Ti (4 h) led to the larger amount of the released hydrogen. Mg_2NiH_4 has a higher dehydriding rate than MgH_2. Lu et al. [3] investigated the hydriding characteristics of an 90 wt.% Mg+10 wt.% Ti alloy prepared by reactive mechanical grinding and hydrogen pulverization. They reported that the addition of titanium efficiently inhibited the oxidation of magnesium during alloying process, improved the hydrogen absorption capacity of 3.63 wt.% as compared with that of Mg (3.36 wt.%), and decreased hysteresis. Palade et al. [7] prepared Mg–Ni–Fe alloys by melt spinning and subsequently ball milling. These alloys showed a better kinetic of hydrogendesorption than similar samples obtained by milling a mixture of MgH_2, Ni, and Fe commercial powders. They insisted that this may be explained by the presence in former samples of Fe at the Mg_2Ni grain boundaries, with catalytic effect on the gas–solid reaction. Meyer and Mendoza-Zélis [8] studied the hydrogen sorption properties of mechanically alloyed $Mg_{1-2x}Fe_xTi_x$ powder mixtures. They concluded that the simultaneous presence of Fe and Ti does not imply a beneficial effect on their catalytic action in powder samples, but Fe alone produce adequate microstructures under a controlled decomposition of mechanically produced Mg_2FeH_6, and Ti/TiH_2 have been demonstrated recently to be a promising alternative.

4. CONCLUSIONS

Reactive mechanical grinding for a longer time (for 8 h), compared with that for 4 h, intensified the effects of reactive mechanical grinding. The effects of of hydriding-dehydriding cycling on the hydriding and dehydriding rates of 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) were very strong from n=1 to n=2. The complete activation of the samples was achieved after about three hydriding-dehydriding cycles. The dehydrided 90Mg-Ni-Fe-Ti (4 h) and 90Mg-Ni-Fe-Ti (8 h) samples after activation contained Mg, $H_{0.3}Mg_2Ni$, MgH_2, MgO, and Fe phases. After activation, 90Mg-Ni-Fe-Ti (4 h) had higher initial hydriding and dehydriding rates and larger quantities of hydrogen absorbed and released for 60 min than 90Mg-Ni-Fe-Ti (8 h). The activated 90Mg-Ni-Fe-Ti (4 h) sample absorbed 5.21 wt.% H for 5 min and 5.67 wt.% H for 60 min at 573 K under 12 bar H_2 and released 1.09 wt.% H for 10 min and 4.72 wt.% H for 60 min at 573 K under 1.0 bar H_2. Prolonged milling (for example, for 8 h) is considered to bring about coalescence of particles which is caused by severe plastic deformation of ductile Mg particles. The stronger effect of hydriding-dehydriding cycling for 90Mg-Ni-Fe-Ti (4 h) may be related to the less compact agglomeration of particles of this sample. The two points (the stronger effect of hydriding-dehydriding cycling and the less compact agglomeration) are believed to lead to the higher initial hydriding and dehydriding rates and the larger quantities of hydrogen absorbed and released for 60 min of 90Mg-Ni-Fe-Ti (4 h) than those of 90Mg-Ni-Fe-Ti (8 h) after n = 2.

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